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(54) PROCESS AND APPARATUS FOR WITHDRAWAL OF A SUSPENSION OF OLEFINIC POLYMERS FROM A CONTINUOUSLY OPERATING REACTOR

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This invention relates to a process for the withdrawal of a suspension of olefinic polymers in continuously operating reactors as well as to an apparatus enabling to carry out this process.

In various continuous processes of polymerization of non-saturated monomers, the elimination or withdrawal of the polymerized products from the polymerization reactor is an essential problem the solution of which directly effects the good operation of the reactor as well as the production of polymers with constant properties.

Presently, according to the usually employed processes, the elimination of polymerized products is very difficult and requires the withdrawal of large quantities of diluent and of reactants which must then be separated from the polymer and treated with a view of their recycling into the polymerization autoclave.

The process and the apparatus of the present invention enable to avoid the majority of these drawbacks.

The object of the present invention resides in providing a process for the withdrawal of a suspension of olefinic polymers in a reactor where the polymerization of olefins is carried out continuously under low pressure in an inert diluent and in the presence of a polymerization catalyst, said process consisting in withdrawing a substantial amount of the crude polymer suspension from the polymerization reactor and pouring it into a decanting zone, then, on the one hand, withdrawing from the polymer enriched broth a portion at least corresponding to the production of the polymer in the reactor, and, on the other hand, recycling to the polymerization reactor the slightly concentrated polymer containing liquid which is extracted from the decanting zone.

A further embodiment of the process described hereinabove comprises to withdraw from the polymer rich broth, apart

from the quantity of the broth corresponding to the production of the polymer in the reactor, an additional portion which is recycled to the reactor.

The invention also concerns a process such as described above, in which there is introduced into the slightly concentrated polymer containing liquid, which is extracted from the decanting zone and recycled into the reactor, at least one of the constituents of the reaction medium and in particular the monomer to be polymerized and, eventually, the balance of the diluent and the chain transfer agent, the catalyst being introduced directly into the reactor.

A preferred embodiment of the process according to the present invention resides in the adjustment of the respective proportions of the polymer enriched broth and of the slightly concentrated polymer containing liquid, escaping from the decanting apparatus, by means of a regulating valve mounted in the recycle conduit of the slightly concentrated polymer containing liquid.

A further object of the present invention is to provide an apparatus for carrying out the above process.

The process and the apparatus of the instant invention are generally applicable to the withdrawal of polymers obtained by continuous polymerization of olefins and, in particular, of ethylene, propylene, 1-butene, 1-pentene, 4-methylpentene-1 and 1,3-butadiene as well as in the copolymerization of olefins among themselves or with diolefins which may be conjugated or not.

The invention is applicable to the withdrawal of polymers and of copolymers obtained in the form of solid particles which are not dissolved in the inert diluent and which result from the polymerization of one or more olefins with the aid of any catalyst suitable for the polymerization under low pressure.

Such catalysts are, for example, the catalysts containing chromium oxide which is at least partially in hexavalent state, deposited on supports such as silicon dioxide, aluminum

oxide and aluminum silicates, or catalysts resulting from the action of reducing agents on metallic compounds of the metals of the groups IV A to VI A of the Periodic Table. Such catalysts are, for example, the combinations of diethylaluminum chloride or of triisobutylaluminum with a titanium tetrahalogenide, titanium trichloride or the complex of the general formula $3TiCl_3$-$AlCl_3$.

There can also be used high activity supported catalysts and particularly those obtained by activating by means of an organometallic compound and preferably a trialkylaluminum or an alkylaluminum halogenide, the product of the reaction between a compound of a transition metal and a solid support such as, for example, a hydroxychloride of a divalent metal, particularly magnesium hydroxychloride, or an inorganic phosphate containing one or more hydroxy groups in the molecule and/or water of crystallization. In this case, the compounds of transition metals are selected particularly from the halogenides, the haloalkoxides and the alkoxides of metals of the groups IV A, V A and VI A of the Periodic Table and more particularly from the derivatives of titanium and vanadium such as $TiCl_4$, $Ti(OC_2H_5)_4$, $Ti(OC_2H_5)_3Cl$, $VOCl_3$, VCl_5 or $VO(OC_4H_9)_3$.

The polymerization is carried out in the presence of a liquid hydrocarbon diluent which is inert at the polymerization conditions and in which the major portion of the polymer is insoluble at the polymerization conditions.

Suitable diluents are paraffinic hydrocarbons such as those having 3 to 8 carbon atoms in the molecule and particularly n-butane, isobutane, n-pentane, isopentane and n-hexane as well as the cyclic saturated hydrocarbons such as the cyclohexane, the cyclopentane and the m thylcyclohexane.

A particularly suitable diluent in certain cases is the monomer its lf maintained in liquid state und r its saturation

pressure.

The sole figure attached to the present specification is a schematic and non-limitative illustration of an apparatus suitable for carrying out the process of the present invention.

The polymerization reactor 1, heated or cooled by means of a double jacket, is provided with a stirrer 2 capable of producing an excellent stirring of the reaction medium, and with at least one inlet tube (not shown) permitting the introduction of the polymerization catalyst.

The tube 3, provided with a pump 4, enables to withdraw in a continuous way a substantial amount of the crude polymer suspension from reactor 1 and to convey it by means of tube 5 into a decanter or separator 6, for example, of a cyclone type.

A portion of the concentrated broth discharged from separator 6 is conveyed back to the polymerization reactor 1 by means of a conduit 7, while the other portion, substantially corresponding to the polymer production of the reactor, is periodically or continuously withdrawn through the valve 9 mounted on outlet tube 8.

On the other hand, the slightly concentrated polymer containing suspension, extracted from separator 6, is conveyed to the polymerization reactor 1 by means of conduit 10 provided with a regulating valve 11 the opening size of which controls the degree of thickening of the concentrated suspension by the adjustment of the respective proportions of the polymer enriched broth and of the slightly concentrated polymer containing liquid escaping from separator 6.

There is also provided a tube 12 and a valve 13 enabling the introduction into the slightly concentrated polymer containing liquid recycled to the reactor, the constituents of the reaction medium and particularly the monomer, the diluent and eventually a chain transfer agent, under the conditi ns where the

polymerization reaction cannot start because of the absence of the solid catalyst in the suspension.

As decanting apparatus, there can be utilized, apart from separators of cyclone type, other classic separators such as continuously operating decanting tanks, centriclone separators or centrifuges.

As polymerization autoclave, there can be used any reactor operating continuously and particularly a closed circuit reactor with the continuous circulation course. Due to the process and apparatus of the present invention, the amounts of non-converted monomer and of the suspension liquid to be treated for recycling into the polymerization reactor are considerably reduced.

The amount of ethylene to be recompressed and purified for recycling into the reactor also becomes very limited.

Furthermore, the apparatus according to the present invention enables to predissolve in the flow of the slightly concentrated polymer containing liquid which is extracted from the separator, the constituents of the reaction medium such as the monomer, the diluent and eventually a chain transfer agent under conditions where the reaction cannot commence because of the absence of a solid catalyst in the suspension.

Such a process is especially effective to avoid large heterogeneities of concentration of the reactants in certain parts of the reactor, which can be responsible for the formation of polymer fractions with undesired properties.

Another embodiment of the device applicable to the process of the present invention consists in utilizing the separator under the conditions whereby it provides a granulometric sorting, so as to separate a concentrated broth containing particles over a certain predetermined granule size. Smaller particles, consisting mainly of grains enriched in catalysts, are then recycled to the reactor by the circuit of the slightly concentrated polymer

containing liquid.

When the operation is carried out in this manner, the productivity of the solid catalyst is improved by avoiding the loss, through premature exit from the reactor, of grains rich in catalyst which have stayed very little in the polymerization reactor.

In such a case, however, it will be necessary to avoid to predissolve the monomer or other reaction components in the slightly concentrated polymer containing liquid which is recycled into the reactor, so as to avoid occurence of polymerization in the recycling pipe.

The invention will now further be illustrated by means of the following non-limitative examples.

<u>Example 1</u>

For the sake of comparison with the process and apparatus of the invention and in order better to bring out its advantages, there has been carried out an experiment of polymerization in which the withdrawal of the polymer suspension and the recycling of the reactants are effected in the usual manner without using the apparatus disclosed by the present application.

There has been used a polymerization reactor for ethylene of a 200 litre capacity, completely full of liquid and thus without gaseous volume, under conditions whereby the concentration of ethylene in the hexane used as diluent is of 3 g per litre of hexane.

The amount of solid catalyst introduced into the reactor is 6 g per hour.

This catalyst is constituted of the reaction product between $Mg(OH)Cl$ and $TiCl_4$, obtained as d scribed in French patent No. 1,448,320. This catalyst is activated by triisobutylaluminum.

The op rating pressure existing in the reactor is of 30 kg/cm^2 and th reaction temperature is 80°C. The normal poly-

ethylene concentration in the reactor is 0.135 kg/l of hexane. The hourly rate of production of polyethylene is 6.750 kg/h.

For a production rate of 6.75 kg/h, the amount of hexane extracted from the reactor and which must be treated before its recycling back into the reactor is of $\frac{6.75}{0.135}$ = 50 l per hour and the amount of non-transformed ethylene is therefore of 3 X 50 = 150 g per hour.

The amount of hexane carried away with the polyethylene is replaced by an equivalent amount, namely 50 l per hour, of fresh solvent.

The amount of ethylene introduced into the reactor is of 6.750 + 0.150 = 6.9 kg per hour. If this ethylene is predissolved in the added fresh solvent, its concentration will be of $\frac{6.9}{50}$ = 0.138 kg/l of hexane.

A solution of such concentration introduced at one point of the reactor will create therein a zone of heterogeneous concentration which will then require a very intense agitation of the reactor in order to reduce the extent and the importance of this high concentration zone.

<u>Example 2</u>

The reactor is provided with an apparatus shown in the appended figure and the operation is carried out under the same polymerization conditions as set forth in Example 1.

The crude polyethylene suspension is drawn off by means of pump 4 which discharges 1135 l of suspension per hour.

This suspension is then introduced into separator 6 where 500 l of hexane per hour are separated in the form of a clear liquid containing practically no polymer.

The concentrated broth is discharged from the separator at a rate of 635 l/h. It consists of 135 kg of polyethylene/h and 500 l of hexane/h. For a production rate, withdrawn through valve 8, equal to that of Example 1, namely 6.75 kg of poly-

ethylene/h, the amount of hexane carried along with the polymer and which must therefore be treated before its recycling, is only of 500 X $\frac{6.75}{135}$ = 25 l/h and the amount of ethylene which has not been transformed is thus of 3 X 25 = 75 g/h.

Furthermore, if the 6.825 kg of ethylene are pre-dissolved in the 500 l/h of the slightly concentrated polymer containing liquid, collected from the separator and intended to be recycled into the reactor, the concentration of this solution will only be of $\frac{6825}{500}$ = 13.6 g of ethylene/l.

This concentration of ethylene in the recycled hexane, which is much closer to the average concentration in the reactor, is acceptable and considerably reduces the risks of local heterogeneity in the reactor.

Of course, the amount of solvent carried along by the polyethylene can be further limited, by increasing the polymer concentration in the suspension coming out of the separator. The limit of such increase in polymer concentration will be determined by the capability of pumping the concentrated suspension for its recycling into the reactor.

It should, of course, be understood that the invention is not limited to the specifically described, exemplified and illustrated embodiments but that many modifications evident to those skilled in the art can be made without departing from the spirit of the invention and the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Process for the withdrawal of a suspension of olefinic polymers in a reactor where the polymerization of the olefins is carried out continuously under low pressure in an inert diluent and in the presence of a polymerization catalyst, comprising withdrawing a substantial amount of the crude polymer suspension from the polymerization reactor and pouring it into a decanting zone, withdrawing a portion of the enriched polymer broth at least corresponding to the production of the polymer in the reactor and recycling to the polymerization reactor the slightly concentrated polymer containing liquid which is extracted from the decanting zone, through a recycling conduit.

2. Process according to claim 1, in which the polymer enriched broth is withdrawn in an amount corresponding to the production of the polymer in the reactor with a further portion being withdrawn for recycling into the reactor.

3. Process according to claim 1, in which into the slightly concentrated polymer containing liquid, which is extracted from the decanting zone and recycled into the reactor, there is introduced at least one of the constituents of the reaction medium.

4. Process according to claim 3, in which the constituent is the monomer to be polymerized.

5. Process according to claim 3, in which the constituents are the monomer to be polymerized, the remainder of the diluent required and a chain transfer agent, th polymerization catalyst being introduced directly into the reactor.

6. Process according to claim 1, in which the respective proportions of the polymer enriched broth and f the slightly concentrated polymer containing liquid escaping from

the decanting zone are adjusted by means of a regulating valve mounted in the recycling conduit for the slightly concentrated polymer containing liquid.

7. Apparatus for polymerization of olefins and withdrawal of the resulting suspension of olefinic polymers comprising: a continuously operating polymerization reactor; a decanter for the crude polymer suspension; means for transfering the crude polymer suspension from the reactor and into the decanter; means for withdrawing polymer enriched broth from the decanter; and a recycling conduit from the decanter to the reactor for recycling into the reactor the slightly concentrated polymer containing liquid.

8. Apparatus according to claim 7, further comprising a recyling conduit from the decanter to the reactor for the polymer enriched broth.

9. Apparatus according to claim 7, in which the recycling conduit for the slightly concentrated polymer containing liquid is provided with a flow regulating valve.

10. Apparatus according to claims 7, 8 or 9, in which the recycling conduit for the slightly concentrated polymer containing liquid is provided with inlet means for introduction of reaction constituents.

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